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Versatile aerosol concentration enrichment system (VACES) for simultaneous in vivo and in vitro evaluation of toxic effects of ultrafine, fine and coarse ambient particles Part II: Field evaluation

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Abstract

This study presents results from a field evaluation of a mobile versatile aerosol concentration enrichment system (VACES), designed to enhance the ambient concentrations of ultrafine (less than 0.18 μm), fine (0–2.5 μm), and coarse particles (2.5–10 μm) for in vivo and in vitro toxicity studies. The VACES may be coupled to an exposure chamber system to assess exposure-dose effects of any one, or all, of ambient aerosol on either human subjects and/or animals. Alternatively, concentrated ultrafine, fine and coarse particles can be directly collected by impaction onto a medium suitable for application to cell cultures for in vitro evaluation of their toxic effects. The enrichment and preservation of ambient ultrafine, fine and coarse particles by size and chemical composition was determined by comparisons made between the VACES and a co-located multistage MOUDI impactor, used as a reference sampler. Furthermore, preservation of the ultrafine fraction is measured by the enrichment based on ultrafine particle numbers, morphological characteristics as well as their elemental carbon (EC) content.

The results suggest that the concentration enrichment process of the VACES does not differentially affect the particle size or chemical composition of ambient PM. The following fractions: (1) mass (coarse and fine PM); (2) number (ultrafine PM); (3) sulfate (fine PM); (4) nitrate (fine PM, after correcting for nitrate losses within the MOUDI); (5) EC (ultrafine PM); and (6) selected trace elements and

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metals (coarse and fine PM), are concentrated very close to the “ideal” enrichment value of 22—thereby indicating a near 100% concentration efficiency for the VACES. Furthermore, ultrafine particles are concentrated without substantial changes in their compactness or denseness, as measured by the fractal dimension analysis. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ultrafine, fine and coarse particle concentrators; Fractal analysis; Particle morphology

1. Introduction

This paper focuses on the application of a mobile versatile aerosol concentration enrichment system (VACES) in an ambient field study, conducted outdoors at Rancho Los Amigos National Rehabilitation Center in Downey (south-central Los Angeles), CA. The VACES (described in greater detail in our companion paper—Kim, Jaques, & Sioutas, 2001) has been designed to simultaneously conduct *in vivo* and *in vitro* exposures to concentration-enriched ambient particles of either one, or all of the coarse, fine and ultrafine size fractions of PM. The VACES consists of three parallel sampling lines (or, concentrators) that separately sample ambient coarse, fine and ultrafine aerosols, each at 110 l min^{-1} . The fine and ultrafine fractions are separated from the air sample and drawn through a supersaturation and condensational growth system. All fractions (i.e., size-selected and enlarged fine and ultrafine, and ambient coarse) are subsequently concentrated with a virtual impactor. The number/mass concentration may be enriched by a factor as great as 33, which is, ideally, determined as a function of the ambient inlet flow rate to the minor flow rate of the virtual impactor (typically between 3.3 and 10 l min^{-1} , depending on the desirable configuration). In the experiments described in this field study, the minor flow of each concentration-enrichment sampling line of the VACES was set at 5 l min^{-1} , thereby resulting in an ideal concentration enrichment of coarse, fine and ultrafine aerosols by a factor of 22.

This field study evaluates the system’s ability to preserve particle mass, number, morphological characteristics as well as chemical composition during the concentration enrichment process. The mobile VACES system has been developed for housing either in stationary trailers used for regional, or a van used for mobile and local source exposure-response measurements. The system is designed to supply concentration-enriched ultrafine, fine and coarse fractions of aerosols to human or animal exposure chambers, or directly collected into a cell culture medium for *in vitro* evaluation of their toxic effects. Particle collection for *in vitro* analysis is accomplished by connecting a BioSamplerTM (Willeke, Lin, & Grinshpun, 1998) to each of the minor flows of the coarse, fine and ultrafine portable concentrators, respectively. Highly concentrated aqueous suspensions can thus be obtained, which can be readily used for exposing cell cultures to ambient particles of all three modes. This direct particle collection also eliminates uncertainties related to incomplete extraction from filter media and preserves the biologically active components of the collected PM (Dick et al., 2000; Zucker, Draz, & Muller, 2000). The reported results, herein, are to substantiate those describing the development and characterization of this system, published as Part I in this series (Kim et al., 2001).

2. Methods

2.1. Field study

The performance of the VACES was evaluated in a field study, conducted outdoors in the facilities of Rancho Los Amigos National Rehabilitation Center in Downey, CA. Situated near the Los Angeles “Alameda corridor”, Downey has some of the highest inhalable particle concentrations (PM_{10}) in the US, very often exceeding the National Ambient Air Quality Standard of $150 \mu\text{g m}^{-3}$. The 25-mile-long Alameda corridor is named after Alameda Street, which joins the coastal area of Long Beach (where a large number of industrial plants and oil distilleries are currently operating) to downtown Los Angeles.

The main goal of the field study was to confirm that the physical or chemical properties of ambient aerosol are preserved during the process of concentration enrichment using the VACES. Measurements of concentration-enriched coarse, fine and ultrafine aerosol fractions were compared to direct ambient measurements made with a co-located Microorifice Uniform Deposit Impactor (MOUDI, MSP Corp. Minneapolis, MN), which was used as a reference sampler. In part, the MOUDI was used because of its high sampling flow rate (i.e., 30 l min^{-1} , about 27% of the VACES), which allows for sufficient sample collection for comparisons with the VACES in relatively short time periods (i.e., 4–6 h). Because each of the sampling lines (or concentrators) of the VACES sample at 110 l min^{-1} , the analytical sensitivity and quantity of particle mass by the VACES, itself, was of less concern. It should be noted, however, that the MOUDI is not a reference sampler for labile species, such as ammonium nitrate and semivolatile organic compounds, and losses of these compounds may occur under conditions of high temperature and low relative humidity (Chang, Sioutas, Kim, Gong, & Linn, 2000).

Instead of using all of the stages of the MOUDI, only those having cutpoints of 10, 2.5 and $0.18 \mu\text{m}$ were used. Thus, the first MOUDI stage ($2.5\text{--}10 \mu\text{m}$) was used as reference sampler for coarse ambient particles, the second stage ($0.18\text{--}2.5 \mu\text{m}$) for the ambient PM accumulation mode, and the last stage (i.e., the after-filter) to determine ambient ultrafine particle concentrations. The MOUDI and VACES coarse and fine (accumulation plus ultrafine) PM concentrations were compared by mass, nitrate, sulfate, trace elements and metals. For these analyses, concentration enriched aerosols were collected on 4.7 cm Teflon filters (Gelman Science, $2 \mu\text{m}$ pore, Ann Arbor, MI), which were placed immediately downstream of the diffusion dryer of the VACES fine and ultrafine particle concentrators, and directly downstream of the minor flow of its coarse concentrator. For direct ambient measurements, the same type of filters were placed in each MOUDI stage and its after-filter unit.

Ultrafine concentrations obtained by means of the VACES and MOUDI were compared based on mass and elemental carbon (EC) concentrations, as EC has been shown to be a predominant ultrafine PM constituent at this ambient site (Sioutas, Kim, Chang, Terrell, & Gong, 2000). For this analysis, quartz filters (Pallflex Corp., Putnam, CT) were placed downstream of the diffusion dryer of the VACES ultrafine concentrator and of the co-located MOUDI after-filter. Organic carbon (OC) may also be a significant constituent of ultrafine PM mass, however positive artifacts due to adsorption of organic gases on the MOUDI’s quartz after-filter (Zhang & McMurry, 1987) may introduce significant bias in the MOUDI-VACES comparisons. In this study, comparisons were based only on the EC fraction of particle-associated carbon, as the

organic carbon fraction may consist of several volatile or semi-volatile compounds, thus data based on the EC fraction are considered to be more robust.

In order to evaluate whether the chemical composition of concentration-enriched ambient particles are effected by using the *in vitro*/BioSampler version of the VACES (Kim et al., 2001), measurements were compared to those made directly onto filters. For the samples collected by means of the BioSampler, only the inorganic ion (i.e., sulfate and nitrate) content of the concentrated aerosols were determined, because of the logistical difficulties associated with weighing (for mass) the BioSampler or analyzing its aqueous extract for EC or OC.

For mass measurements, Teflon filters were weighed before and after each field tests using a Mettler 5 Microbalance (MT 5, Mettler-Toledo Inc., Highstown, NJ), under controlled relative humidity (e.g., 40–45%) and temperature (e.g., 22–24°C) conditions. Filters were weighed immediately at the end of each experiment as well as after a 24 h equilibration time period. Laboratory and field blanks were used for quality assurance. Filters and filter blanks were weighed twice in order to increase precision. In case of a difference of more than 3 µg between consecutive weighings, a filter was weighed a third time. The Teflon filters were then analyzed by means of ion chromatography to determine the concentrations of particulate sulfate and nitrate. Trace element and metal concentrations for ambient and concentrated PM were determined by analyzing the MOUDI and VACES Teflon filters by means of inductively coupled plasma mass spectroscopy (ICP/MS). This analysis was conducted by the Monitoring and Laboratory Division of the California Air Resources Board.

The EC concentrations were determined by thermo-analysis. A slice of approximately 0.2 cm² from each filter was placed in a platinum boat containing MnO₂. The sample was acidified with an aliquot of HCl and heated to 115°C to dehydrate the sample, and form CO₂ as an index of particle-associated carbon. The boat was then inserted into a dual zone furnace, where MnO₂ oxidized organic carbon at 550°C and elemental carbon at 850°C. A Flame Ionization Detector (FID) converted the CO₂ combustion product to CH₄ for detection. This analytical method is more elaborately described by Fung (1990).

2.2. *Effect of condensation and evaporation in the VACES on agglomerate structure*

A significant fraction of the ultrafine particles in the Los Angeles atmosphere are agglomerate structures, mainly emitted from diesel and other high temperature sources. Agglomerate structures have higher surface areas than spherical particles with the same equivalent diameter; agglomerate transport properties in both gas and liquid phases differ from spherical particles as well (Friedlander, 2000). These differences in surface area and transport properties may influence the biochemical effects of inhaled ultrafine particles. For these reasons, it is important to know whether condensation and evaporation that precede aerosol concentration in the VACES affect the morphological properties of the ultrafine particles.

Atmospheric ultrafine particles and those concentrated by the VACES were sampled using the low-pressure impactor (LPI) in the environment of the UCLA campus, in west Los Angeles. Measurements for the ambient air and concentrated particles were made within minutes of each other. Concentrated ultrafine aerosols generated by the VACES were sampled after they were dried by diffusion. The LPI is an eight-stage single-jet impactor equipped with a critical orifice that maintains a flow rate of 1 l min⁻¹ under the appropriate pressure drop (Hering,

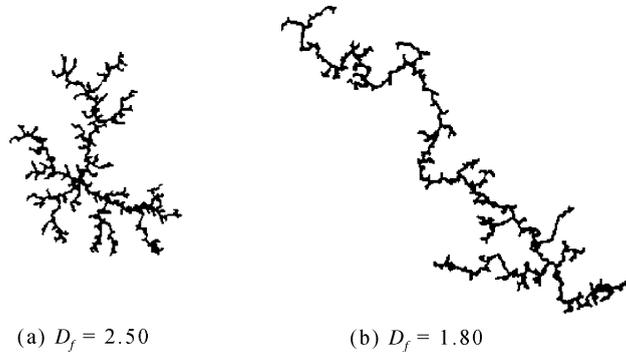


Fig. 1. Structure and fractal dimension of agglomerates produced by two computer simulation algorithms (after Schaefer, 1988). Diffusion-limited aggregation was simulated for two subcases, (a) particle-cluster aggregation and (b) cluster-cluster aggregation. Particle-cluster aggregation refers to the release of single particles, which attach to a growing cluster by Brownian diffusion. In cluster-cluster aggregation, agglomerates of primary particles are released and collide by Brownian motion.

Flagan, & Friedlander, 1978). The stages have 50% efficiency cutoffs in aerodynamic diameter of 4.0, 2.0, 1.0, 0.5, 0.26, 0.11, 0.075, and 0.05 μm for stages 1–8, respectively. The particles were collected on a nickel grid. To minimize the effects of particle bounce, only one stage at a time had a grid attached for sampling; the grid is secured at the center of a 25 mm diameter glass stage, while the other glass stages are coated with Apiezon grease. Air was drawn through the impactor by a vacuum pump for 5 min per stage for the concentrated aerosols and 10 min for the ambient air samples. Analysis was done for changes in structural characteristics of the agglomerate fraction. The agglomerates analyzed were comprised of 11–542 primary particles. These agglomerates were collected on stages 7 and 8, which have particle aerodynamic diameter ranges of 0.075–0.11 and 0.05–0.075 μm , respectively. Transmission Electron Microscope (TEM) photomicrographs of the grids were taken using a JEOL 100CX and 2000FX TEM at a magnification of 10^5 . The morphology of ultrafine particles ($d_p < 0.10 \mu\text{m}$) was characterized using the fractal concept applied to TEM micrographs. More details on fractal analysis can be found in Xiong (2000).

Experiments and simulations have shown that the fractal concept can be applied to aggregates of nanometer primary particles (Forrest & Witten, 1979; Witten & Sander, 1981). In applying the fractal concept, the fractal dimension and the prefactor for both ambient and concentrated particles were calculated. The fractal dimension (D_f) is a measure of the stringiness of the agglomerate and the prefactor (A) is a measure of denseness of the agglomerate. An agglomerate with the same fractal dimension as another may have a higher prefactor if it contains a higher primary particle overlap. Agglomerates produced by computer simulation algorithms help in the understanding of structure and fractal dimension (Friedlander, 2000). Fig. 1 illustrates two examples for diffusion-limited aggregation. An agglomerate with a chain-like structure has a lower fractal dimension than a more compact, spheroidal one. The structure of an agglomerate with a D_f value of 1 is a linear chain of primary particles. For a D_f value of 2 the agglomerate structure is a two-dimensional arrangement of closely packed primary particles with six nearest neighbors; and the structure for a D_f value of 3 is a three-dimensional closely packed sphere.

Table 1
Coarse ambient particle concentrations determined with the MOUDI and the VACES

Ambient ($\mu\text{g m}^{-3}$)	VACES ($\mu\text{g m}^{-3}$)	Enrichment factor
(a) <i>Sulfate</i>		
1.0	20.8	21.6
1.4	22.0	15.2
0.8	16.6	20.8
1.4	34.0	24.3
2.1	58.5	28.5
	Average	22.1
	SD	4.9
(b) <i>Nitrate</i>		
4.68	83.85	17.91
6.43	135.87	21.13
3.71	57.80	15.58
6.78	155.77	22.98
5.41	118.28	21.86
	Average	19.90
	SD	2.6

The agglomerate fractal dimension and prefactor arise from the following relationship (Weber, Thorne, & Friedlander, 1995):

$$N_p = A \left(\frac{R_g}{R_0} \right)^{D_f}, \quad (1)$$

where D_f is the fractal dimension, N_p is the number of primary particles in the aggregate, A is the fractal prefactor or structural coefficient, R_0 is the average primary particle radius, R_g is the radius of gyration. The radius of gyration can be calculated using the relation: $[(1/M) \sum (m_i r_i^2)]^{1/2}$, where m_i is the mass of the i th primary particle, M is the total mass given as $\sum m_i$, and r_i is the distance of the i th primary particle from the center of mass. The fractal dimension and prefactor of randomly sampled ambient and concentrated particles were obtained by plotting the number of primary particles positioned radially from the center of mass to the radius of the gyration of the agglomerate. The fractal dimension was determined from the slope and the prefactor was determined from the inverse log of the intercept of the least squares fit line.

3. Results and discussion

In each of the sampling lines of the VACES, coarse, fine and ultrafine particles were concentrated from an intake flow of 110 to a minor flow of 5 l min^{-1} . Thus, the ideal concentration enrichment factor for any chemical PM species is expected to be 22. Results from these field tests are summarized in Tables 1 and 2 and in Figs. 2–7. In each figure, the concentrations determined by the VACES are compared to those determined by the MOUDI; the coordinates are fit by a linear regression and the tightness-of-fit by correlation coefficients. The slopes of

Table 2

Ultrafine PM number concentrations upstream and downstream of the 0.18 μm cutpoint impactor and downstream of the ultrafine concentrator of the VACES. All concentrations are averaged over 30 min sampling time

VACES particle number concentration (particles cm^{-3})	Particle number concentration downstream of the 0.18 μm impactor (particles cm^{-3})	Ambient particle number concentration (particles cm^{-3})	Ratio of downstream-to-upstream the 0.18 μm impactor concentration (particles cm^{-3})	Concentration enrichment
551429	26714	32185	83%	20.7
801429	35000	43166	86%	22.9
420000	23000	31750	74%	18.3
600000	29857	33666	85%	20.1
648571	30428	35714	85%	21.3
795714	38285	45142	84%	20.8
574286	26880	31523	86%	21.4
		Average	0.83	20.8
		SD	0.042	1.41

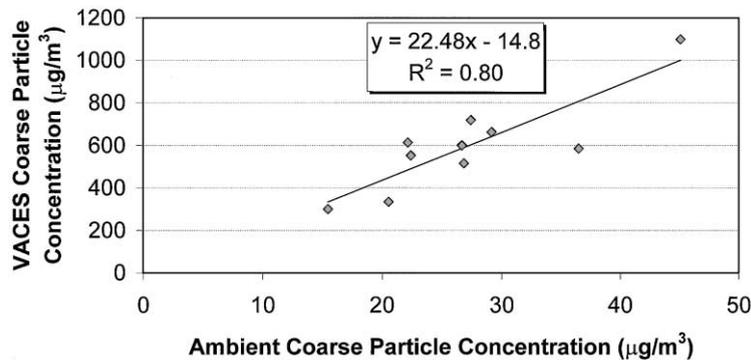


Fig. 2. Plot of ambient (MOUDI) and VACES coarse particle concentrations.

the regression lines thus provide an average estimate of the overall concentration enrichment factor obtained by means of the VACES for a given PM fraction and species. Table 1a presents the sulfate and Table 1b the nitrate content of the coarse fraction of ambient (MOUDI) and concentration-enriched ambient aerosol (VACES). The corresponding enrichment factor (defined as the ratio of the VACES coarse aerosol concentration to that of the MOUDI) is presented for each of five samples. Fig. 2 presents paired measurements of ambient coarse aerosol mass concentrations obtained by the MOUDI versus those concentrated by the VACES.

As indicated by the slope of the regression line in Fig. 2, the average concentration enrichment of the VACES is 22.5 (± 3.8), thus, very close to the ideal value of 22. The rather limited data obtained for coarse particle sulfate and nitrate (Table 1a and b, respectively) also indicate a close agreement between the VACES and MOUDI, with the concentration enrichment factors for sulfate and nitrate of 22.1 (± 4.9) and 19.9 (± 2.6), respectively. The limited data for these inorganic ion measurements are due to the very low nitrate and sulfate content within the coarse

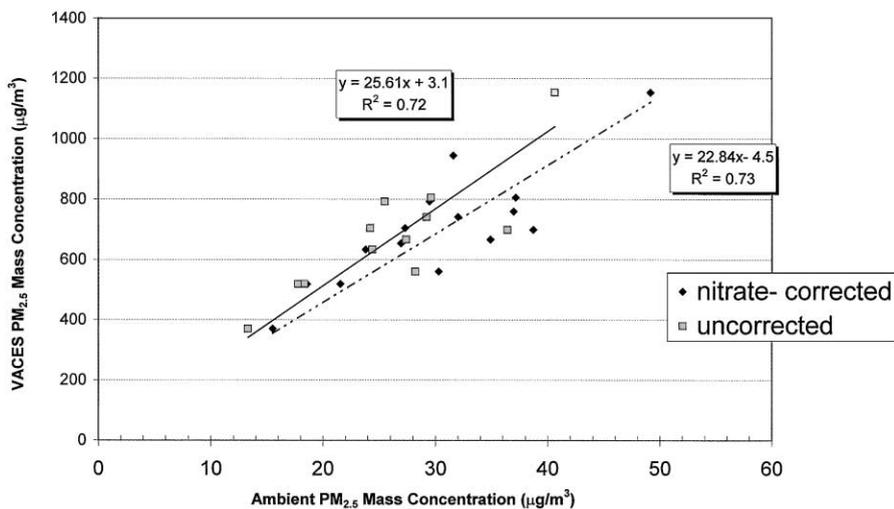


Fig. 3. Plot of ambient (MOUDI) and VACES $PM_{2.5}$ mass concentrations.

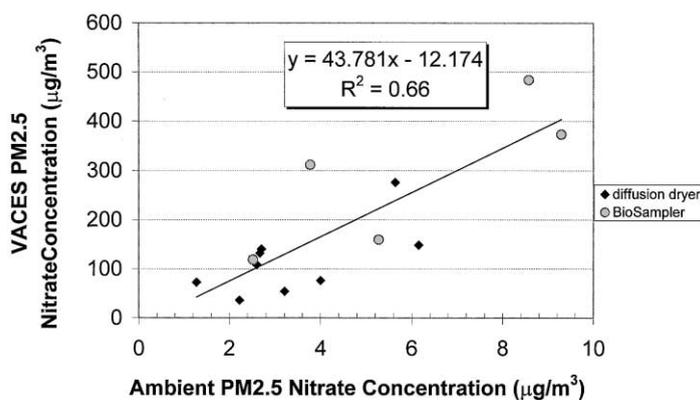


Fig. 4. Plot of ambient (MOUDI) and VACES $PM_{2.5}$ nitrate concentrations.

fraction of PM in the specific Los Angeles location. Thus, a greater level of uncertainty exists in the measurements made with the MOUDI (which samples at about one fourth of the flow rate of each sampling line of the VACES). Nevertheless, the overall agreement between the VACES and the MOUDI for coarse particle mass, sulfate, and nitrate is near “ideal”.

Fig. 3 shows the $PM_{2.5}$ mass concentrations measured by the MOUDI and VACES. The overall concentration enrichment obtained for the fine PM mode is slightly higher (25.6 ± 3.7) than the ideal value of 22, as indicated by the slope of the regression line. As further discussed below, this may be due, in part, to losses of volatile species, such as ammonium nitrate, from the MOUDI substrates in the lower stages. Evidence of this phenomenon was not the case for the coarse PM collected in the upper stage of MOUDI, where the pressure drop is much lower than the smaller cutpoint stages. Moreover, coarse particulate nitrate in south and western Los Angeles

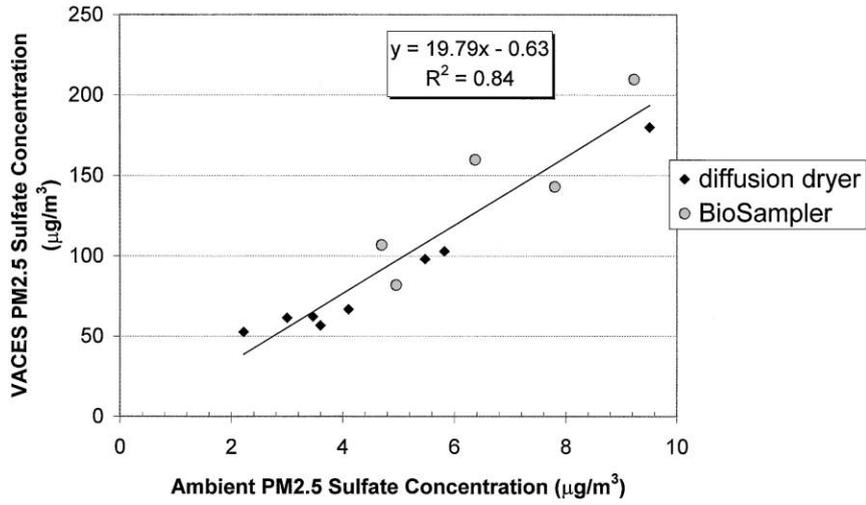


Fig. 5. Plot of ambient (MOUDI) and VACES PM_{2.5} sulfate concentrations.

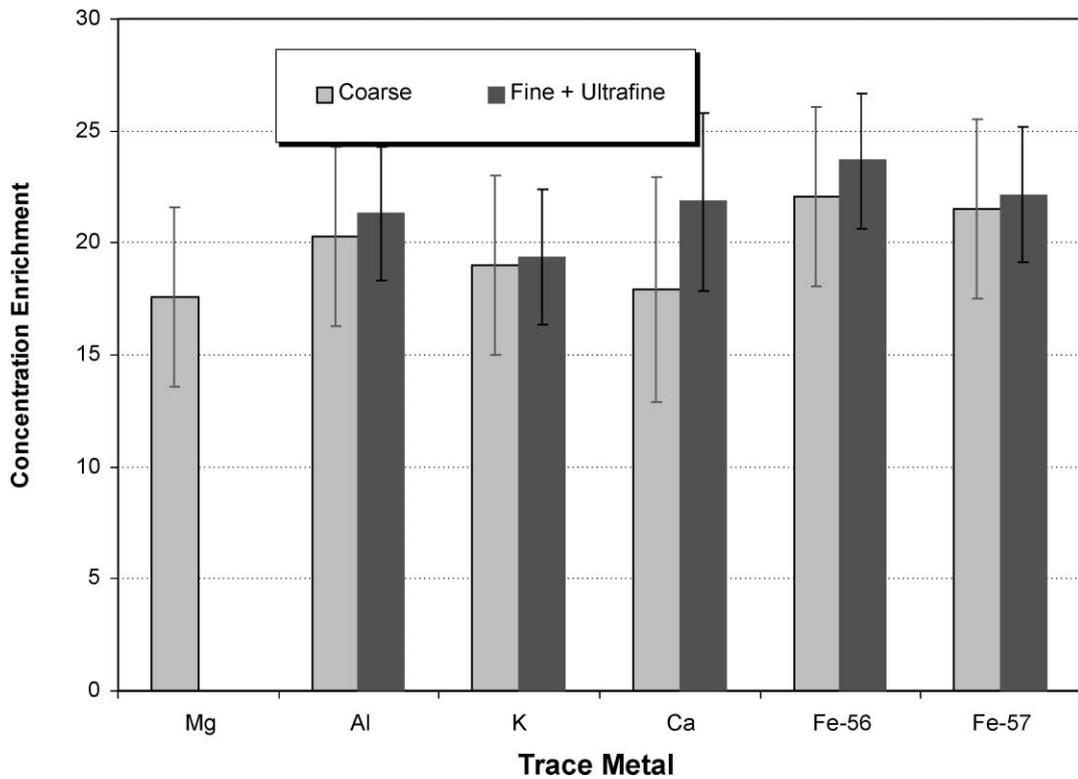


Fig. 6. Concentration enrichment of selected trace elements and metals in coarse and fine ambient particles. Average and standard deviation values correspond to seven field experiments.

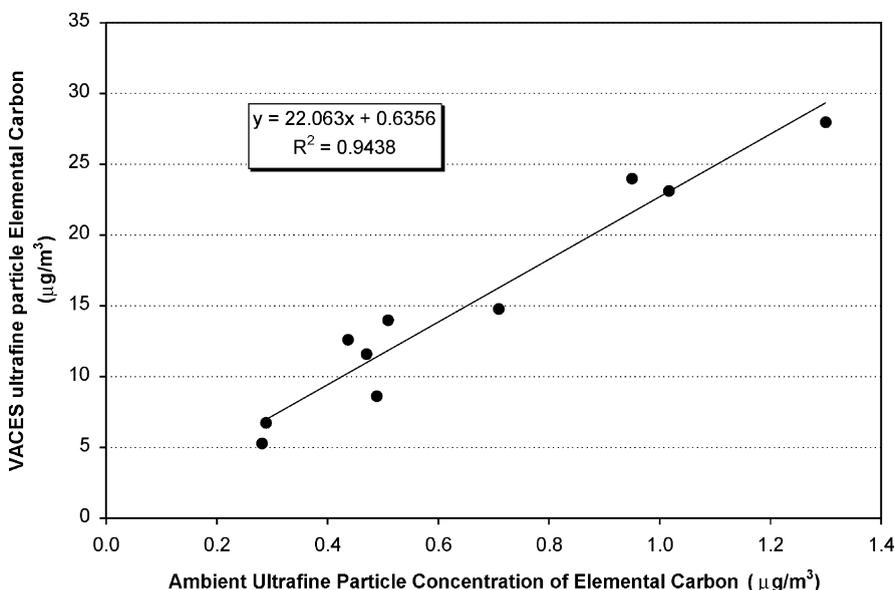


Fig. 7. Plot of ambient (MOUDI) and VACES ultrafine elemental carbon (EC) concentrations.

(i.e., areas closer to the coast) is mostly associated with stable sodium nitrate (Noble & Prather, 1996).

These experiments were conducted during the months of May and June, 2000, with temperatures averaging $32 (\pm 3)^\circ\text{C}$ and low relative humidity values (i.e., about 35% or less). These conditions have been shown to favor loss of ammonium nitrate from impactor samplers (Chang et al., 2000; Zhang & McMurry, 1987) due to the higher values of the dissociation constant of ammonium nitrate. For this temperature and humidity range, the study by Chang et al. (2000), which was conducted at the same site, presented that the total losses of nitrate from the MOUDI averaged between 40% and 60%. Furthermore, a previous study by Kim, Chang, Kim, and Sioutas (2000) showed that concentration enrichment through a smaller-scale portable fine PM concentrator, which has similar design parameters to that of the VACES (in terms of aerosol saturation and cooling temperatures), occurs without any measurable loss of particulate nitrate, despite heating and saturation of the aerosol to about 35°C . In that earlier study, ambient nitrate concentrations were determined by means of the Harvard/EPA Annular Denuder System (HEADS;), used as the reference sampler. The HEADS measures total particulate nitrate without losses (Koutrakis, Wolfson, Slater, Brauer, & Spengler, 1988). Thus, any bias in the enrichment factor of ammonium nitrate above the “ideal” value (i.e., inlet flow divided by minor flow), may be due to its losses in the MOUDI, and concerns of a negative bias, due to potential ammonium nitrate losses in the saturation–condensation segment of the VACES, which may be masked by this effect, is discussed below.

Ammonium nitrate dissociates to ammonia and nitric acid, with its dissociation constant increasing exponentially with temperature. However, the dissociation constant decreases sharply as the relative humidity (RH) exceeds 90–95% (Stelson & Seinfeld, 1982). For example, at 50°C and at $\text{RH} = 95\%$, the dissociation constant of ammonium nitrate is approximately 7 ppb^2 ,

which is also the value of the dissociation constant at 18°C, and RH = 50%. Therefore, despite the increase in the aerosol temperature (which would have increased, exponentially, the value of the dissociation constant), aerosol exposure to high water vapor conditions in the VACES seems to prevent nitrate losses due to volatilization.

These conclusions are further supported by the results shown in Fig. 4, where the PM_{2.5} nitrate concentrations measured by means of the MOUDI are compared to those measured by the VACES. The average concentration enrichment based on nitrate is 43.8 (±20.3), roughly twice the value of the ideal concentration enrichment. Given that nitrate losses depend significantly on parameters that vary quite randomly, such as temperature, humidity and overall particle concentration, the MOUDI-to-VACES agreement should be highly variable, which is indicated by the somewhat lower correlation coefficient ($R^2 = 0.66$) of the VACES vs. MOUDI data.

By comparison, the concentration enrichment obtained for the non-volatile fine particulate sulfate (shown in Fig. 5) was 19.8 (±4.3) and thus in very good practical agreement to the ideal value of 22. The above results confirm that the disparity between the ideal and actual concentration enrichment factors based on nitrate is due to sampling artifacts of the MOUDI.

The results plotted in Fig. 5 also show that there is no significant difference ($p = 0.38$) in the sulfate-based concentration enrichment values obtained with the *in vivo* version of the VACES (in which concentrated particles are dried by diffusion and collected on filters) and the *in vitro* version (in which particles are collected by the BioSampler). The concentration enrichment obtained by means of the BioSampler was 21.2 (±3.5), compared to 18.9 (±2.5) obtained using the diffusion-dried concentrated particles collected on Teflon filters. Given the high values and random nature (due to meteorological factors) of nitrate losses within the MOUDI during the sampling period, a similar comparison of the *in vivo* and *in vitro* versions of the VACES based on fine particulate nitrate would be difficult, if not meaningless.

The MOUDI fine PM mass concentrations were corrected for nitrate losses as follows:

$$PM_{\text{corr}} = PM_{\text{MOUDI}} + 1.29 \left(\frac{NO_{3,\text{VACES}}}{22} - NO_{3,\text{MOUDI}} \right), \quad (2)$$

where $NO_{3,\text{VACES}}$ and $NO_{3,\text{MOUDI}}$ are the nitrate concentrations measured by the VACES and MOUDI, respectively, and PM_{MOUDI} is the total MOUDI fine PM mass concentration determined gravimetrically. The above equation assumes that all nitrate found in the fine particulate mode is associated with ammonium nitrate. The corrected values of the MOUDI mass concentrations are also shown in Fig. 3, along with the adjusted concentration enrichment factor. The nitrate-adjusted concentration enrichment factor becomes 22.8 (±3.4), thus very close to the ideal enrichment value of 22. These results imply that the discrepancy between the PM_{2.5} mass concentrations between VACES and MOUDI can be entirely attributed to the difference in the nitrate concentrations measured by these two systems.

The results of Fig. 4 also indicate that the overall impact of nitrate losses from the MOUDI substrates on the mass concentration determined by the MOUDI is rather small. This is because ammonium nitrate accounts on the average for 30–40% of the total PM_{2.5} mass concentration at Downey, CA (Sioutas et al., 2000). Thus, even if nitrate losses are as high as 50%, the overall difference between the uncorrected and nitrate-adjusted mass concentrations is not substantial, as indicated by the data presented in Fig. 3.

Results from the concentration enrichment obtained for selected trace elements and metals are shown in Fig. 6. Due to the low ambient concentrations of trace elements and metals measured by the MOUDI, quantifiable concentration enrichment values were obtained only for the following metals: Mg (coarse PM only), Al, K, Ca, and two iron isotopes (i.e., ^{56}Fe and ^{57}Fe). Measurable amounts of Zn, Cu, Ni and Mn were also identified in the filters connected to the fine concentrator of the VACES, but not in the corresponding MOUDI stages. The average and the standard deviation values of concentration enrichment shown in Fig. 6 correspond to seven (of 10) field experiments. In the remaining four three field tests, the ambient concentrations of the aforementioned metals were either comparable to the blank content of the Teflon filters or lower than the ICP/MS limit of detection (defined as three times the standard deviation of the laboratory blank filters).

The data in Fig. 6 indicate that the Al, K, Ca, ^{56}Fe and ^{57}Fe content of fine and ultrafine PM is enriched by a factor of 21.2 (± 4), 19.4 (± 3.3), 22.1 (± 3.8), 24.3 (± 3.1) and 22.4 (± 3.4), respectively. Similarly, the Mg, Al, K, Ca, ^{56}Fe and ^{57}Fe content of coarse PM is enriched by a factor of 18.6 (± 4.2), 20.4 (± 3.3), 19.3 (± 3.8), 18.3 (± 4.2), 22.1 (± 3.4) and 21.6 (± 3.5), respectively. These concentration enrichment values are also close to the ideal enrichment value of 22, thereby indicating that the concentration enrichment process preserves the concentrations of these elements and trace metals in both coarse and fine PM.

Table 2 shows the concentration enrichment achieved by the ultrafine concentrator of the VACES based on particle counts, using a condensation particle counter (3022 CPC; TSI Inc., St. Paul, MN). The first column of Table 2 shows the ambient concentration based on particle counts; the second column shows that the number concentration, measured immediately downstream of the 0.18 μm cutpoint impactor; and the third column corresponds to the particle number concentrations measured immediately downstream of the diffusion dryer of the ultrafine concentrator of the VACES. The fourth column shows the ratio of particle counts downstream to that upstream of the 0.18 μm impactor, indicating that about 84% of ambient particle counts are associated with particles smaller than that size. The final column of Table 2 shows the concentration enrichment obtained for ultrafine particles, defined as the ratio of the count-based concentration downstream of the VACES to that downstream of the 0.18 μm impactor. The overall concentration enrichment for ultrafine particles was 20.8 (± 1.4), thereby indicating that ultrafine particles are concentrated with very high efficiency by the VACES.

Earlier investigations of the size distribution of ambient elemental carbon (EC) in Los Angeles (Venkataraman & Friedlander, 1994), showed that EC displays a bimodal size distribution, with peaks within the 0.05–0.12 μm (mode I) and 0.5–1.0 μm (mode II) size ranges. Mode I was attributed to primary emissions from combustion sources while mode II was attributed to the accumulation of secondary reaction products on primary aerosol particles. Mode I contained 75–85% of EC, by mass, in the Los Angeles air basin during the summer season. Therefore, the performance of the ultrafine particle concentrator of the VACES was characterized by further comparing EC concentrations obtained with the VACES to those measured in the afterfilter of the MOUDI (collecting 0–0.18 μm particles).

Results from these field comparisons are shown in Fig. 7. Similar to the results based on particle count and mass concentrations, a high level of comparability resulted between the VACES and MOUDI EC concentrations, with the average concentration enrichment factor being

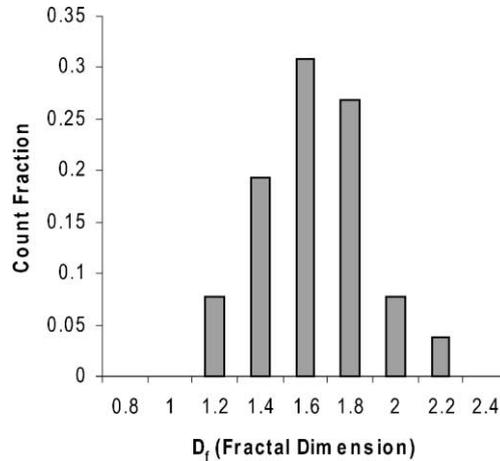


Fig. 8. Fractal dimension distribution for agglomerates from the VACES. The count mean D_f value was found to be between 1.6 and 1.8. Samples were taken at the Center for Health Sciences at UCLA using a low-pressure impactor (LPI).

22.2 (± 2.3). Ultrafine particle EC concentrations obtained by means of the MOUDI and VACES are also very highly correlated ($R^2 = 0.94$).

It should be noted that the ability of the VACES to enrich the concentrations of all particles in the fine mode (including its ultrafine component) is a particularly important feature of this technology, as it enables inhalation toxicologists to conduct exposures to any selected sub-range of $PM_{2.5}$. For example, previous studies in California presented the presence of two sub-modes within the accumulation mode of ambient PM (Hering et al., 1978). One mode peaks at around $0.2 \mu\text{m}$, consisting mainly of gas-to-particle reaction products, such as carbonaceous PM and the other peaks at about $0.7 \mu\text{m}$, mainly associated with hygroscopic PM species, such as ammonium sulfate and ammonium nitrate. These observations have been confirmed by our recent year-long measurements at the facility of Rancho Los Amigos in Downey (Sioutas et al., 2000). By thus placing a conventional impactor upstream of the fine concentrator of the VACES, having for example a $0.35 \mu\text{m}$ cutpoint, inhalation studies could be conducted to ultrafine PM plus the elemental and organic carbon content of the accumulation mode, however, without the majority of its sulfate and nitrate constituents.

3.1. Effect of condensation and evaporation in the VACES on agglomerate structure

Changes in agglomerate structure were investigated by comparing the fractal dimension and the prefactor of concentrated ultrafine particles from the VACES to ambient particles. Our results, shown in Figs. 8 and 9, indicate that the concentrated and ambient particles show very similar morphology. The fractal dimension and prefactor values were determined for a total of 38 ambient and 39 concentrated ultrafine particles. Figs. 8 and 9 show the fractal dimension value distributions for concentrated and ambient aerosols, respectively. The count median fractal dimension is very similar (between 1.6 and 1.8) for both concentrated and ambient particles. Furthermore, the average prefactor for the particles collected from the VACES is 2.73 and for the

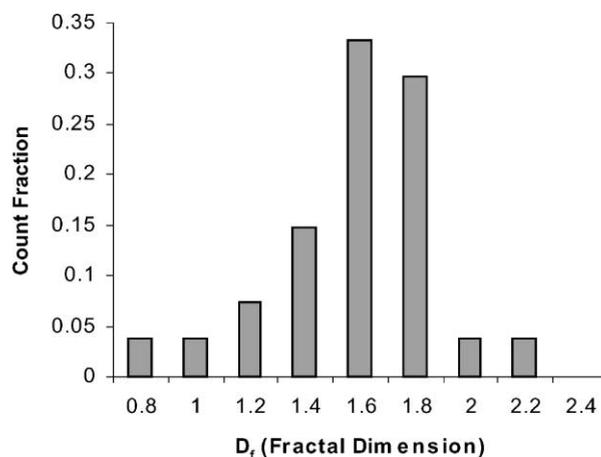


Fig. 9. Fractal dimension distribution for agglomerates sampled from the ambient aerosol. The count mean D_f value was found to be between 1.6 and 1.8. Samples were taken at the Center for Health Sciences at UCLA using a low-pressure impactor (LPI).

atmospheric is 2.83. Higher prefactor values are typically associated with denser agglomerates, but similar to the fractal dimension, the difference between the concentrated and atmospheric aggregate prefactor is not significant.

Previous studies suggest that chain agglomerates may become more compact when subjected to condensation and evaporation processes (Colbeck, Appleby, Hardman, & Harrison, 1990; Hallet, Hudson, & Rogers, 1989; Wells, Venn, & Heard, 1976). A study shows that for diesel chain-agglomerate particles the fractal dimension increased from 1.56 to 1.76 and 1.40 to 1.54 for mid and low sulfur fuel after condensation and evaporation processes (Huang, Turpin, Piphon, Kittelson, & McMurry, 1994). However, in our study the average fractal dimension showed practically no change in value following condensation and evaporation in the VACES. An explanation is that in the study by Huang et al. (1994) the particles underwent up to three cycles of condensation and evaporation while in our study the particles only went through one cycle. We can therefore conclude that the condensation and evaporation process used with the VACES is effective in concentrating the sampled ultrafine particles but causes little change in the compactness or denseness of the particles, as measured by the fractal dimension and prefactor. However, both the sources of the fractal-like structures and associated trace gases may affect this phenomenon. Since the measurements were made for one sampling site, more experiments will need to be made in different sites to make these conclusions generalizable.

4. Summary and conclusions

This study focuses on a field evaluation of a versatile particle concentration enrichment system (VACES), which is capable of concurrently enriching the concentration of ambient coarse, fine, and ultrafine particles. The field study was conducted outdoors in the facilities of Rancho Los Amigos National Rehabilitation Center in Downey (south-central Los Angeles), CA. The coarse,

fine and ultrafine particle concentrations of the VACES were compared to direct concurrent measurements made with a co-located MOUDI. Comparisons between the VACES and MOUDI for coarse and fine PM are based on particle mass, sulfate, nitrate and selected trace element and metal concentrations. For ultrafine PM (here defined as those having aerodynamic diameter smaller than a 0.18 μm), the VACES number concentrations is compared to those of a co-located Condensation Particle Counter, whereas the preservation and concentration enrichment of the elemental carbon (EC) content is determined by comparing VACES concentrations to those of the MOUDI within this size fraction.

The field characterization of the versatile coarse, fine, and ultrafine concentrators indicates that concentration enrichment is differentially affected by particle size or chemical composition. For either coarse or fine particles, the concentration enrichment factors based on mass, sulfate, nitrate (after correcting for nitrate losses of the MOUDI), and selected trace elements and metals were very close to the ideal enrichment value of 22. The experiments, additionally, indicated that volatile species such as ammonium nitrate are preserved throughout the concentration enrichment process. Furthermore, concentration enrichment obtained for ultrafine particle counts suggests that no particle coagulation occurs during the enrichment process. Finally, ultrafine EC concentrations obtained with the VACES were about 22 times higher than those obtained with the MOUDI, thereby indicating that ultrafine PM are concentrated without loss, with a nearly 100% collection efficiency by this system. In addition, detailed morphological examination of ambient and concentrated ultrafine particles indicated that ultrafine particles are concentrated without substantial changes in their compactness or denseness.

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